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Procedures for the Analysis of Metals, Alloys, and Other Materials of Research

Part 5 - An Investigation of the Chemical Analysis of Cadmium-Zinc Arsenide

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PREVIOUS REPORTS IN THIS SERIES

"Part 1 – Procedures for the Chemical Analysis of Copper-Base Alloys," O. R. Gates and O. Mylting, NRL Report 6357, Mar. 1966

"Part 2 – Determination of Silver and Indium in Magnesium-Base Alloys, Lead in Indium, and Zirconium in Hafnium," O. R. Gates and E. J. Brooks, NRL Report 6427, Sept. 1966

"Part 3 – A Spectrophotometric Procedure for the Determination of Trace Amounts of Cobalt in Ferrous Alloys," O. R. Gates, NRL Report 6857, Dec. 1968

"Part 4 – Spectrophotometric Procedures for the Determination of Ions Formed Within Stress-Corrosion Cracks," O. R. Gates, NRL Report 6948, Oct. 1969

CONTENTS

ABSTRACT

Cadmium-zinc arsenide has been analyzed by a combination of chemical and instrumental techniques. After the initial removal of arsenic by distillation, cadmium and zinc are determined by a combined gravimetric and atomic absorption spectrophotometric procedure or by a polarographic procedure.

The experimental procedures for determining each of the three major constituents are given in detail. Methods used for checking the effectiveness of their respective separation are also discussed.

PROBLEM STATUS

This is the fifth in a series of progress reports; work on the problem is continuing.

AUTHORIZATION

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PROCEDURES FOR THE ANALYSIS OF METALS, ALLOYS, AND OTHER MATERIALS OF RESEARCH

Part 5 - An Investigation of the Chemical Analysis of Cadmium-Zinc Arsenide

INTRODUCTION

This is the fifth in a series of reports concerning progress in the development of chemical methods by the Analytical Chemistry Branch of the Central Materials Research Activity.

Recent studies on crystalline cadmium-zinc arsenide have revealed its sensitivity to infrared radiation, which suggest its possible use as a detector material in this region of the electromagnetic spectrum. These crystals have also been observed to possess laser properties.

Accurate analytical data for the three major constituents of these crystals were obtained on crystals weighing approximately 0.3 g and of varying atomic ratios to correlate the observed physical data with the elemental composition. These data were compiled by the use of wet chemical, polarographic, and atomic absorption spectrophotometric techniques.

Although wet-chemical treatment to remove arsenic is necessary with any of these techniques, the polarographic determination of cadmium and zinc as major constituents has considerable appeal because well-defined diffusion current patterns are obtainable for both elements. However, in major constituent analysis, the slightest instrumental or interpretive discrepancy may reveal itself as a relatively large deviation when converted to percentage. Many instrument makers claim accuracies to ±2% of the amount of a given element present. At the 50% level, a result could vary between 49 and 51% and remain within the specified instrumental accuracy limits.

The determination of cadmium and zinc as major constituents by atomic absorption spectrophotometry was not attempted because the same accuracy limits were predicted to apply to it and also because it does not permit the wide sensitivity range obtainable polarographically.

Since the scientists preparing and working with the crystals were explicitly interested in the accurate chemical analysis of the three major constituents, various wet-chemical facets have been investigated. The following combined wet-chemical and atomic absorption spectrophotometric technique has been evolved that is capable of providing good analytical data: The arsenic is reduced to the trivalent state with hydrazine sulfate, distilled as the trichloride, and titrated with a standard iodine solution. Working with an aliquot of the solution remaining in the distilling flask, the cadmium and zinc are separated with hydrogen sulfide and determined as their respective sulfates. The cadmium and zinc residues, after being weighed, are redissolved, diluted to definite volumes, and examined by atomic absorption spectrophotometry to determine, and make proper adjustments for, the amount of zinc in the cadmium residue and the amount of cadmium in the zinc residue.

Aliquots of the solution remaining in the distilling flask may also be analyzed spectrophotometrically to determine the effectiveness of the arsenic distillation and analyzed polarographically to provide additional cadmium and zinc data.

Using a 1M ammonium chloride-ammonium hydroxide solution as the supporting electrolyte and a gelatin solution to suppress the zinc maxima, excellent polarographic diffusion current patterns are obtained for both cadmium and zinc.

To appraise and compare techniques, only data for the synthetic standard sample solutions are included in this report. At least two of these solutions were analyzed with each series of crystals tested.

METHODS OF ANALYSIS

Preliminary Sample Treatment

Reagents*

Arsenite Standard Stock Solution (N = 0.1) – National Bureau of Standards arsenious oxide (9.892 g) is dissolved in 80 ml of water containing 20 g of sodium hydroxide. After diluting to about 500 ml with water and saturating with carbon dioxide, the solution is transferred to a 2000-ml volumetric flask, diluted to the mark, and mixed thoroughly. One milliliter of this solution contains 0.00374 g of arsenic.

Cadmium Standard Stock Solution (1 ml = 0.0100 g of Cd) – High-purity cadmium (4.7500 g) is dissolved in 25 ml of water and 25 ml of nitric acid. The solution is diluted with 30 ml of water, boiled about 3 min, cooled to room temperature, transferred to a 500-ml volumetric flask, diluted to the mark with water, and mixed thoroughly.

Zinc Standard Stock Solution (1 ml = 0.0050 g of Zn) – High-purity zinc (2.5000 g) is dissolved in 10 ml of water and 10 ml of nitric acid. The solution is diluted with 30 ml of water, boiled about 3 min, cooled to room temperature, transferred to a 500-ml volumetric flask, diluted to the mark with water, and mixed thoroughly.

Procedure

Using appropriate aliquots of the standard stock solutions, two synthetic standards (closely resembling the samples to be tested) should be included with each series of analyses.

The cadmium-zinc arsenide crystal, usually in the form of a disk weighing 0.3000 to 0.6000 g, is transferred to a 500-ml Erlenmeyer flask containing 15 ml of nitric acid and 20 ml of sulfuric acid. The flask is covered with a watch glass and placed on a steam bath overnight. The sample is usually well disintegrated, if not completely dissolved, by the next morning. With the cover slightly ajar, the flask is placed on an asbestos pad on a hot plate, and the contents are carefully evaporated until fumes of sulfur trioxide are evolved. With the cover still ajar, nitric acid is completely removed by placing the flask on an asbestos-centered wire gauze and heating it vigorously with a Fisher burner until the sulfuric acid refluxes quietly from the cover glass; the fuming process is hastened if the flask is surrounded by an asbestos jacket that is about 5 inches in diameter and 5.5 inches tall.

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*Unless otherwise specified, only reagent-grade chemicals are used throughout this report.

The cover and flask, after cooling, are rinsed several times with water. The arsenic is completely reduced to the trivalent state by adding 0.3 g of hydrazine sulfate* and repeating the evaporating[†] and fuming procedure as directed in the preceding paragraph. The flask is again cooled to room temperature and rinsed with water before being transferred to the distillation flask.

Distillation of Arsenic

Apparatus

A Scherrer (1)[‡] or modified Scherrer all-glass distilling apparatus may be used. The modified apparatus used for this work is shown in Fig. 1.

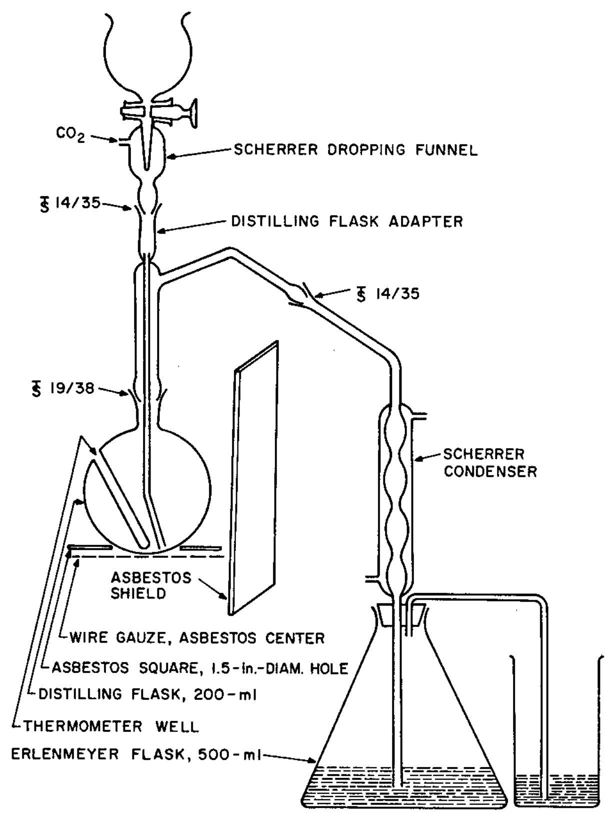

Fig. 1 - Modified Scherrer distilling apparatus

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*Hydrazine sulfate was chosen over flowers of sulfur as a reductant because its excess is completely destroyed during the fuming process. Other reductants, such as cuprous chloride and ferrous sulfate, contaminate the sample solution with undesirable anions. In dilute solutions, arsenic is not completely reduced by boiling with sulfurous acid.

†During the evaporating process, the reducing action of hydrazine sulfate is so strong that much of the arsenic appears to be reduced to a dark, finely divided metallic state which redissolves to form arsenious sulfate as sulfur trioxide fumes begin to form.

‡The Scherrer all-glass distilling apparatus may be obtained from the Scientific Glass Apparatus Co., Bloomfield, N.J. The distilling flask for the modified apparatus may also be obtained from the same company.

Reagent

A lecture-bottle cylinder of carbon dioxide gas is suitable.

Procedure

After the solution containing the cadmium, zinc, and arsenic (together with three or four rinsings of the Erlenmeyer flask) is transferred to the distilling flask, the apparatus is assembled on a ring stand, with the distilling flask resting on an asbestos-centered wire gauze surmounted with a 5-inch-square asbestos pad containing a circular 1.5-inch hole at or near its center. The wire gauze is supported by a ring attached to the ring stand about 16 inches above the base. This permits the ready adjustment of the height of a Fisher burner that is attached to the stand with a clamp. Attached also to the stand is a clamp that supports the Scherrer condenser.

In assembling the apparatus, each glass joint is wetted with water and securely fastened to its counterpart. Before attaching the dropping funnel, it is recommended that the bore of the stopcock plug and the dropping tube extending below it be filled with water to facilitate the subsequent addition of hydrochloric acid. The flow of cooling water for the condenser is adjusted, a 300°C thermometer is inserted in the thermometer well of the distilling flask, and the flow of carbon dioxide through the distilling flask is adjusted to about one bubble per second (later, the flow rate may require adjustment to prevent the solution in the receiving flask from backing into the condenser during the distillation). The Scherrer condenser tip is extended about 5 inches through a two-hole rubber stopper. Also inserted through the rubber stopper is a delivery tube, bent as shown in Fig. 1. A 500-ml Erlenmeyer flask containing about 100 ml of water is attached to the rubber stopper so the condenser tip extends into the water; the bent delivery tube is immersed to about the same level in approximately 100 ml of water in a beaker (see p. 3).

With the asbestos shield suspended between the burner and the condenser, 15 ml of hydrochloric acid is added to the dropping funnel, and heat is applied to the distilling flask with a Fisher burner. The distillation process may be hastened by shielding the distillation flask and the adapter with asbestos. When the temperature reaches 190°C, the burner is lowered about 3 or 4 inches to prevent overheating. At 200°C, the dropwise addition (about one drop every 5 seconds) of hydrochloric acid is started and maintained throughout the next 20 to 30 minutes as the temperature is held between 200° and 220°C. When all of the hydrochloric acid has been added, the heating is discontinued and the system is allowed to cool to near room temperature. The carbon dioxide flow is maintained until about 15 ml of water is slowly and carefully added to the distilling flask through the dropping funnel. The glass joints of the adapter are loosened; the smaller male part being rinsed into its condenser counterpart, the larger male part being rinsed into its distilling flask counterpart. Then the inner walls of the adapter are rinsed, collecting the rinsings in the distilling flask; and the inner walls of the condenser are rinsed, collecting the rinsings in the receiving flask.

The solutions in the receiving flask and beaker are reserved for the analysis of arsenic.

The solution in the distilling flask is transferred to a 300-ml beaker and diluted to 150 ml with water. It is then filtered through a Whatman-40 11-cm filter paper into a 250-ml volumetric flask. After washing four times with hot 5% sulfuric acid and four times with hot water, the flask is cooled to room temperature, diluted to the mark, mixed thoroughly, and reserved for the analysis of cadmium, zinc, and possibly traces of arsenic. If the residue from the ignited filter paper weighs more than 0.3 mg, it should be examined by emission spectroscopy.

Volumetric Analysis of Arsenic

The volumetric analysis of arsenic is directly applicable to samples containing between about 3 and 160 mg of arsenic. The upper limit may be extended by titrating an appropriate aliquot of the distillate reserved for the analysis of arsenic. In the crystals tested, the arsenic content varied between 24 and 200 mg.

Reagents

Iodine Standard Solution ($N \approx 0.1$) – Resublimed iodine (25.4 g) is dissolved in 70 ml of water containing 80 g of potassium iodide, diluted to 2 liters with water, and mixed thoroughly. The solution is then standardized against a standard sodium arsenite solution.

Potassium Iodide Solution (10%) – Potassium iodide (10 g) is dissolved in 100 ml of water. This solution is prepared fresh as needed.

Sodium Arsenite Standard Solution (1 ml = 0.00374 g of As) – Use the same arsenite standard stock solution prepared for the preliminary sample treatment.

Sodium Bicarbonate Powder

Sodium Hydroxide Solution (40%) – Sodium hydroxide (400 g) is added to 500 ml of water and stirred intermittently until dissolved, then diluted to 1 liter.

Starch Solution (1%) – Soluble starch (1 g) is wetted with 5 ml of water and added to 95 ml of hot water that has just been boiled.

Procedure

A small piece of congo red test paper is added to the reserved arsenic distillate contained in the 500-ml Erlenmeyer flask; a piece is also added to the solution contained in the beaker*. Each solution is neutralized with the sodium hydroxide, then made just acid to the test paper with 1:1 sulfuric acid. After cooling, 4 g of sodium bicarbonate powder is carefully added. Continuing with each solution individually, 5 ml of the potassium iodide solution and 3 ml of the starch solution are added; then the solution is titrated immediately with the standard iodine solution to the blue starch indicator endpoint.

Spectrophotometric Analysis of Arsenic

Spectrophotometry provides a means for determining trace amounts of undistilled arsenic that could appear as a contaminant in the analysis of cadmium. Less than a microgram of arsenic may be determined by this technique.

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*The solution in the beaker may be added to the 500-ml Erlenmeyer flask to make a single iodine titration. However, the separate titration of the solution in the beaker provides a measure of the amount of arsenic trichloride that escaped collection in the Erlenmeyer flask.

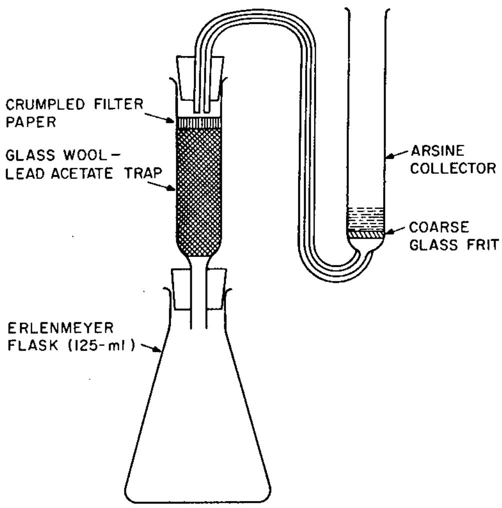

Fig. 2 - Arsine generator

Apparatus

Arsenic Generators - A series of arsine generators* similar to the one shown in Fig. 2 is used for this work.

Spectrophotometer and Accessory Equipment

Reagents†

Dilute Arsenic Standard Stock Solution (1 ml = 187 μg of As) - Ten milliliters of the 0.1N sodium arsenite solution is diluted to the mark in a 200-ml volumetric flask and mixed thoroughly.

Dilute Arsenic Standard Solution (1 ml = 3.74 μg of As) - Ten milliliters of the dilute arsenic standard stock solution is diluted to the mark in a 500-ml volumetric flask and mixed thoroughly.

Lead Acetate Solution (10%) - Lead acetate trihydrate (10 g) is dissolved in 100 ml of water and mixed thoroughly.

Potassium Iodide Solution (15%) - Potassium iodide (15 g) is dissolved in 100 ml of water containing a pellet of sodium hydroxide.

Pyridine - ACS grade

Silver Diethyldithiocarbamate (2,3&4)‡ Solution (0.0.5%) — Silver diethyldithiocarbamate (1 g) is dissolved in 200 ml of pyridine.

Stannous Chloride Solution (40%) - Stannous chloride dihydrate (40 g) is dissolved in 100 ml of concentrated hydrochloric acid.

Zinc Metal, Granular (20 Mesh)

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*All-glass arsine generators may be obtained from the Fisher Scientific Co., Pittsburgh, Pa.

†Except for the arsenic standard solutions, the arsenic content of these reagents must be very low.

‡Silver diethyldithiocarbamate may be obtained from the Fisher Scientific Co., Pittsburgh, Pa.

Procedure

The apparatus is prepared for assembly by soaking glass wool in the lead acetate solution and inserting the wetted fibers into the tube that is to be attached to the Erlenmeyer flask. However, before assembling the apparatus, the tube is dried and a thin plug of crumpled filter paper is inserted over the glass wool. It is then securely connected to the arsine collector. Unless inadvertently damaged, the lead acetate trap may be used repeatedly for many arsine evolution experiments. A 10-ml aliquot* of the cadmium-zinc solution reserved in the 250-ml volumetric flask from the distillation of arsenic is transferred to a 125-ml Erlenmeyer flask. Then 25 ml of water, 5 ml of hydrochloric acid, 2 ml of the 15% potassium iodide solution, and 8 drops of the 40% stannous chloride solution are added. The flask is swirled and allowed to stand 15 minutes.

After adding exactly 5 ml of the silver diethyldithiocarbamate-pyridine solution to the arsine collector tube, it is held or suspended to prevent any loss of the chromogenic reagent solution until 3 g of the zinc metal is added to the Erlenmeyer flask. The lead acetate trap with the arsine collector is immediately attached to the Erlenmeyer flask. With the assembly secured in an upright position with a clamp, the reaction is permitted to proceed for 30 minutes.

Each arsine collector tube is disengaged and its contents transferred to a clean, dry absorption cell. The transmittances of the samples and standards are measured in the spectrophotometer that has been properly adjusted with the blank at a wavelength of 560 nm. The undistilled arsenic content of the various sample solutions is established from a calibration curve prepared with data obtained for the standards.

Gravimetric Analysis of Cadmium

Depending on the sample weight and the constituent percentages, the cadmium in the crystals analyzed was found to vary between 120 and 550 mg. It should be possible to obtain fairly accurate data with as little as 3 mg of cadmium. Although no noticeable difficulty was encountered with samples containing 500 mg of cadmium, working with smaller aliquots is advisable when the samples contain larger amounts of cadmium.

Apparatus

Platinum or porcelain crucibles with a capacity of 30 ml may be used; platinum crucibles are preferred.

Reagent

A lecture-size cylinder of C.P. hydrogen sulfide is suitable.

Procedure

A 200-ml aliquot of the solution in the 250-ml volumetric flask from the distillation of arsenic is transferred to a 300-ml Berzelius beaker. The beaker is placed on an asbestos pad on a hot plate, and the solution is evaporated, without boiling, until fumes of sulfur trioxide are evolved. After cooling slightly, 2 ml of nitric acid is added and the

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*Standards containing about 3 and 12 mg of arsenic and a blank should be included with each series of analyses.

evaporation continued to near dryness*. Exactly 4 ml of concentrated sulfuric acid is added from a burette. The beaker is rinsed with water, and the solution is diluted to 30 ml and boiled several minutes to insure the dissolution of all salts. The volume is adjusted to 250 ml with water. Hydrogen sulfide is bubbled through the solution for 20 min, paper pulp is added, and the gassing is continued for another 10 min. The precipitate, containing largely cadmium and small amounts of zinc, is filtered through a Whatman-40, 12.5-cm filter paper and washed about 4 times with 0.5% sulfuric acid solution that has been saturated with hydrogen sulfide, collecting the filtrate and washings in a 600-ml beaker†. The filtrate and washings are reserved for the analysis of zinc.

The filter paper containing the precipitate is returned to the precipitating beaker. If traces of the precipitate are observed on the funnel, they should be collected on a small piece of damp filter paper and returned to the precipitating beaker also. By adding 15 ml of nitric acid, 5 ml of perchloric acid, and 5 ml of sulfuric acid and evaporating to fumes, initially on a hot plate and finally on an asbestos-centered wire gauze over a Fisher burner until sulfuric acid refluxes freely from the cover glass, the organic matter is destroyed and the cadmium is converted to the sulfate. After cooling to room temperature, the beaker is carefully rinsed down and the solution is evaporated to dryness without a cover glass and without boiling. The cooled salts are wetted with 5 ml of hydrochloric acid, rinsed with water, and heated gently until dissolved. The solution is then evaporated to a volume of about 1 ml and transferred quantitatively, by rinsing, to a tared platinum or porcelain crucible. Ten drops of 1:1 sulfuric acid are added, and the solution is evaporated to dryness, ignited carefully for several hours at 500°C, cooled in a desiccator, and weighed. It is then reserved for the evaluation of its zinc content by atomic absorption spectrophotometry.

Analysis of Zinc in Cadmium Residue by Atomic Absorption Spectrophotometry

Working at a volume of 100 ml, the spectrophotometric technique can detect 1 to 100 μg of zinc in the cadmium sulfate residue; the optimum range of zinc concentration is 20 to 80 μg of zinc in 100 ml of solution. Through further dilution, the upper limit may be increased as required. Gravimetrically, the total zinc contamination begins to have significance at or above the 100 μg level.

Apparatus

A Fisher (Jarrel-Ash) atomic absorption spectrophotometer with a zinc hollow-cathode tube is used for this work. Using an air-hydrogen atomizing flame, the zinc resonance line at 2138.6 A is measured with the spectrophotometer.

Reagents

Cadmium Matrix‡ Standard Solution (1 ml = 1000 μg of Cd) – Transfer 25.0 ml of the cadmium standard stock solution prepared for the preliminary sample treatment to a 500-ml volumetric flask, dilute to the mark, and mix thoroughly.

*This evaporation is included to provide a reproducible acid adjustment.

†During the washing process, some of the cadmium precipitate may appear in the filtrate. A proper adjustment for this will be made later via atomic absorption spectrophotometry.

‡This solution is used to adjust the zinc standards to contain approximately the same amount of cadmium as is contained in the sample solution to be tested.

Dilute Zinc Standard Solution (1 ml = 100 μg of Zn) – Transfer 10.0 ml of the zinc standard stock solution prepared for the preliminary sample treatment to a 500-ml volumetric flask, dilute to the mark, and mix thoroughly.

Procedure

The cadmium sulfate residue reserved from the gravimetric analysis of cadmium is wetted with ten drops of 1:1 sulfuric acid and digested with about 5 ml of water until the salts are dissolved. It is then transferred to a 100-ml volumetric flask, diluted to the mark, and mixed thoroughly. This solution may contain 0.045 to 0.450 g of cadmium and 10 to 10,000 μg of zinc. A quick preliminary run by atomic absorption spectrophotometry will indicate the approximate zinc concentration and the dilution required to provide the optimum zinc range of 0.20 to 0.80 μg per milliliter. Then an aliquot of the sample solution is diluted accordingly with water.

A blank and four standards are prepared to cover the optimum zinc range and to contain approximately the same amount of cadmium that is present in the diluted sample solution. Cadmium, at or above 50 μg per milliliter, depresses zinc absorbance. Therefore, it is necessary to adjust the cadmium content of the zinc standards to within ±20% of the cadmium content of the sample solution to be tested. The sample and standard solutions are siphoned into the flame and their respective zinc absorbances measured. The zinc content of the sample solution is established from a calibration curve prepared with the measured zinc absorbances of the standard solutions.

Gravimetric Analysis of Zinc

Depending on the sample weight and the constituent percentages, the zinc in the samples analyzed was found to vary between 10 and 213 mg. It should be possible to obtain good data with as little as 3 mg or as much as 500 mg of zinc.

Apparatus

Platinum or porcelain crucibles with a capacity of 30 ml may be used; platinum crucibles are preferred.

Reagents

Formic Acid Mixture – Formic Acid (100 ml) is diluted to 485 ml with water, and further diluted with 15 ml of ammonium hydroxide.

Hydrogen sulfide – A lecture-size cylinder of the C.P. hydrogen sulfide gas is suitable.

Tartaric Acid Solution (25%) – Tartaric acid (25 g) is dissolved in about 70 ml of water, then diluted to 100 ml with water and mixed.

Procedure

The filtrate and washings obtained from the cadmium sulfide separation during the gravimetric analysis of cadmium are evaporated to a volume of about 150 ml to expel most of the hydrogen sulfide. After adding 2 ml of the tartaric acid solution, the solution is neutralized to methyl red with ammonia and made just acid with hydrochloric acid. To adjust the pH, 25 ml of the formic acid mixture is added; then the solution is diluted to 250 ml and heated until it just begins to boil. Hydrogen sulfide is bubbled through the solution for 15 min, a little paper pulp is added, and the gassing is continued for 10 more minutes.

At the end of the gassing period, the solution is heated gently to coagulate the precipitate, then filtered through a Whatman-40, 12.5-cm filter paper containing paper pulp. The precipitating beaker is rinsed and the precipitate washed with hydrogen sulfide-saturated solution containing 25 ml of the formic acid mixture and 975 ml of water. The paper and precipitate are returned to the precipitating beaker. Twenty milliliters of nitric acid, 5 ml of perchloric acid, and 5 ml of sulfuric acid are added to the beaker. Then the solution is evaporated until sulfur trioxide fumes are evolved. The beaker is then heated over an asbestos-centered gauze with a Fisher burner until sulfuric acid refluxes quietly from the cover glass. After cooling to room temperature, the beaker and cover are carefully rinsed with water, and the solution is evaporated to dryness without a cover glass and without boiling. The cooled salts are wetted with 5 ml of hydrochloric acid, and the solution is evaporated to a volume of about 1 ml, then transferred to a tared platinum or porcelain crucible. Ten drops of 1:1 sulfuric acid are added, and the solution is evaporated carefully, without boiling, to dryness. The crucible containing the zinc sulfate is carefully ignited for several hours at 500°C, cooled in a desiccator, weighed, then reserved for the evaluation of its cadmium content by atomic absorption spectrophotometry.

Analysis of Cadmium in Zinc Residue by Atomic Absorption Spectrophotometry

Working at a volume of 100 ml, atomic absorption spectrophotometric analysis may be used to evaluate 1 to 120 μg of cadmium in the zinc sulfate residue; the optimum range of cadmium concentration is 20 to 100 μg of cadmium in 100 ml of solution. Through further dilution the upper limit may be increased as required. Gravimetrically, the total cadmium concentration begins to have significance at or above the 100 μg level.

Apparatus

A Fisher (Jarrel-Ash) atomic absorption spectrophotometer with a cadmium hollow-cathode tube is used for this work. Using an air-hydrogen atomizing flame, the cadmium resonance line at 2288.0 A is measured with the spectrophotometer.

Reagents

Dilute Cadmium Standard Solution (1 ml = 100 μg of Cd) – Transfer 5 ml of the cadmium standard stock solution prepared during the preliminary sample treatment to a 500-ml volumetric flask, dilute to the mark, and mix thoroughly.

Zinc Matrix* Standard Solution (1 ml = 1000 μg of Zn) – Transfer 100 ml of the zinc standard stock solution prepared during the preliminary sample treatment to a 500-ml volumetric flask, dilute to the mark, and mix thoroughly.

*This solution is used to adjust the cadmium standards to contain approximately the same amount of zinc as is contained in the sample solution to be tested.

Procedure

The zinc sulfate residue reserved from the gravimetric analysis of zinc is wetted with ten drops of 1:1 sulfuric acid and digested with about 5 ml of water until the salts are dissolved. It is then transferred to a 100-ml volumetric flask, diluted to the mark, and mixed thoroughly. This solution may contain 0.001 to 0.150 g of zinc and 20 to 600 μg of cadmium. A quick preliminary check by atomic absorption spectrophotometry will indicate the approximate cadmium concentration and the dilution required to provide the optimum cadmium range of 0.20 to 1.00 μg per milliliter. Then an aliquot of the sample solution is diluted accordingly with water.

A blank and four standards are prepared to cover the optimum cadmium range and to contain approximately the same amount of zinc that is present in the diluted sample solutions. Zinc, at or above 50 μg per milliliter, depresses cadmium absorbance slightly. Therefore, it is necessary to adjust the zinc content of the cadmium standards to within $\pm 20\%$ of the zinc content of the sample to be tested. The sample and standard solutions are siphoned into the flame, and their respective cadmium absorbances measured. The cadmium content of the sample solution is established from a calibration curve prepared by plotting measured cadmium absorbance versus cadmium concentration of the standard solutions.

Polarographic Analysis of Cadmium and Zinc

Although polarography is applicable over a wide molar concentration range, greater precision is generally obtained at the 10^{-3} to 10^{-4} M level. With the solution in the distilling flask adjusted to a volume of 250 ml, a further 10-fold dilution is required to bring the cadmium and zinc concentration to the optimum range.

Apparatus

The recording polarograph used for this work was a Leeds and Northrup Electro-Chemograph with an H-type combination saturated calomel reference electrode and electrolysis cell.

Reagents

Ammonium Chloride-Ammonium Hydroxide Solution (2M) – Ammonium chloride (107 g) is dissolved in 860 ml of water and diluted with 140 ml of ammonium hydroxide.

Cadmium-Zinc Polarographic Calibrating Solution – A 10-ml aliquot of the cadmium standard stock solution and a 20-ml aliquot of the zinc standard stock solution, both prepared during the preliminary sample treatment, are transferred to a 500-ml Erlenmeyer flask and carefully evaporated with 20 ml of sulfuric acid until fumes of sulfur trioxide are copiously evolved. After cooling, the solution is carefully diluted, again cooled, transferred to a 500-ml volumetric flask, diluted to the mark with water, and mixed thoroughly. One milliliter of this solution contains 200 μg each of cadmium and zinc.

Gelatin Solution (0.04%) – USP gelatin powder (0.04 g) is wetted with 5 ml of water and mixed with 95 ml of freshly boiled water until dissolved.

Procedure

A 5-ml aliquot of each of the cadmium-zinc solutions reserved in the 250-ml volumetric flasks from the distillation of arsenic is transferred to a 50-ml volumetric flask, neutralized with ammonium hydroxide using a small piece of congo red test paper, and made just acidic with hydrochloric acid. The solution is diluted with 25 ml of the 2M ammonium chloride-ammonium hydroxide supporting electrolyte solution and 2 ml of the gelatin solution, then diluted to the 50-ml mark with water and mixed thoroughly.

Calibration curve standards are prepared by transferring 0-, 5-, 10-, and 20-ml aliquots of the cadmium-zinc polarographic calibrating solution to appropriately numbered 50-ml volumetric flasks. Each is treated as directed in the preceding paragraph.

Before electrolyses are begun, the instrument is turned on and allowed to become stabilized. The electrolysis cell is rinsed thoroughly with water, and, with the tip of the dropping electrode immersed in water, the mercury column is adjusted so a droplet of mercury forms and falls about every 5 seconds.

To perform an electrolysis*, the cell is flushed with about three portions of the solution to be tested with nitrogen bubbling through the liquid in the cell at the rate of about one bubble per second. Then the cell is filled sufficiently with the same solution to cover the frit connecting the saturated calomel reference electrode and also the tip of the dropping-mercury electrode capillary tube. After bubbling nitrogen through the solution for 5 minutes, all stopcocks are closed and the electrolysis is started at -0.4 V, in reference to the saturated calomel electrode (SCE). As the voltage scan crosses the -0.5 V line, the recorder is started and the polarogram is recorded through the -0.5- to -1.7-V range†. The electrolyzing current is turned off, and the cell is emptied and made ready for the next solution to be tested.

The diffusion currents of the polarographic calibrating solutions are plotted against their respective cadmium and zinc contents to prepare curves for evaluating the diffusion currents of the solutions to be tested. Figure 3 shows a damped polarogram of a sample containing 81 μg of cadmium and 84 μg of zinc per milliliter of test solution.

DISCUSSION

Polarographic Versus Wet-Chemical Analysis

Polarography was chosen to obtain instrumental data because it applies so amenably to the analysis of the cadmium and zinc encountered in this report. Table 1 shows the data obtained on synthetic standard sample solutions polarographically and gravimetrically, the latter by the combined wet-chemical and atomic absorption spectrophotometric technique. Although greater accuracy for cadmium and zinc appears to be obtainable gravimetrically, carefully performed polarographic analyses would meet many major constituent analytical requirements.

Isolation and Determination of Arsenic

To prevent arsenic from acting as a subsequent interferent, it is especially important that it be quantitatively removed before proceeding with the analysis of cadmium and

*It is recommended that the order of the electrolyses progress from the blank through the low-content cadmium-zinc solutions to the high-content cadmium-zinc solutions.
†In this work the half-wave potentials for cadmium and zinc occur respectively at -0.84 and -1.39 V (vs SCE).

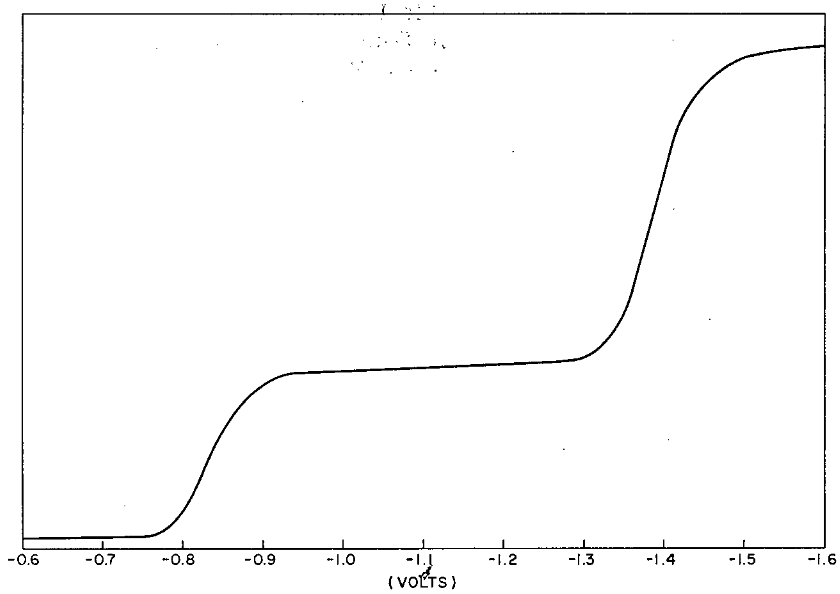

Fig. 3 - Polarogram of a sample containing 81 μg of cadmium and 84 μg of zinc per milliliter of test solution. The moderately damped polarographic trace was obtained with the sensitivity set at 30 μA full-scale deflection.

zinc. Distillation offers an effective means of separating arsenic, and if distilled as the trichloride, it may be titrated directly with a standard iodine solution. After the distillation of arsenic, the solution remaining in the distilling flask is reserved for the wet-chemical or polarographic determination of cadmium and zinc; an aliquot of it may also be used to determine the effectiveness of the arsenic distillation.

Although spectrophotometric tests have established that no significant amounts of arsenic remain in the distilling flask after distillation, initial titrations of the distillate revealed a significant arsenic discrepancy. For example, 25.3 ml of the standard iodine solution was required to titrate directly a 25-ml aliquot of the 0.1N sodium arsenite solution, whereas only 24.6 ml of the standard iodine solution might be needed to titrate the arsenic distilled from a similar aliquot of the sodium arsenite solution. Distillation efficiency was first suspected. It was for this reason that the silver diethyldithiocarbamate spectrophotometric technique was incorporated into the study. Table 2 shows the effectiveness of the arsenic distillation procedure.

In the distillation of arsenic using hydrochloric acid as the carrier, the arsenic must be in the trivalent state; the distillation is only about 5% efficient for pentavalent arsenic. Using hydrobromic acid as the carrier, the distillation is 100% efficient for arsenic in either valence state. However, the arsenic is not directly titratable in the hydrobromic acid medium. Attempts to use it were not very satisfactory.

The arsenic discrepancy was finally traced to incomplete retention of the arsenic trichloride in the distillate. In Table 3, the column under beaker shows typical amounts of arsenic that escaped collection in the Erlenmeyer flask. The Erlenmeyer flask-beaker combination was added to the distillation setup to provide an improved means of collecting the distilled arsenic trichloride.

Table 1
Chemical and Polarographic Data Obtained for Cadmium and Zinc on Synthetic Cd-Zn-As Standards

Taken (g)	Cadmium				Taken (g)	Zinc			
	Found					Found			
	Chemically*		Polarographically			Chemically*		Polarographically	
	Grams	Percent	Grams	Percent		Grams	Percent	Grams	Percent
			0.0950	100.0				0.0420	100.0
0.0950	0.0956	100.6	0.0955	100.5	0.0420	0.0432	102.8	0.0410	97.6
			0.0970	102.2				0.0425	101.2
0.0950	0.0955	100.5	0.1020	107.5	0.0420	0.0422	100.5	0.0400	95.3
			0.0986	103.8				0.0435	103.5
0.0950	0.0935	98.5	0.0960	101.0	0.0420	0.0420	100.0	0.0405	96.4
			0.0975	102.6				0.0430	102.4
0.0950	0.0955	100.5	0.0955	100.5	0.0420	0.0423	100.6	0.0415	98.8
			0.1925	101.4				0.0415	98.8
0.1900	0.1899	99.9	0.1930	101.5	0.0420	0.0417	99.3	0.0415	98.8
			0.1970	103.6				0.0425	101.2
0.1900	0.1903	100.2	0.1925	101.4	0.0420	0.0416	99.1	0.0410	97.6
			0.2000	103.0				0.2150	102.4
0.1944	0.1960	100.8	0.2000	103.0	0.2100	0.2060	98.1	0.2225	106.0
			0.2075	103.5				0.2146	102.2
0.2007	0.2015	100.5	0.2037	101.5	0.2100	0.2070	98.6	0.2220	105.6

*Data include atomic absorption spectrophotometric adjustments.

Table 2
Arsenic Contained in the Distilling Flask

Arsenic Present (g)	
Prior to Distillation	After Distillation
0.0748	0.000037
0.0748	N.D.*
0.0748	N.D.
0.0748	0.000012

*Not detected.

Table 3
Typical Arsenic Distillation Recoveries

Arsenic Distilled (g)	Arsenic Found (g)		
	In Erlenmeyer Flask	In Beaker	Total
0.0935	0.0910	0.0026	0.0936
0.0935	0.0928	0.0007	0.0935
0.0935	0.0924	0.0009	0.0933
0.0935	0.0917	0.0015	0.0932

The Chemical Separation of Cadmium and Zinc

The quantitative chemical separation of cadmium and zinc is quite tedious by some methods. One of the more commonly used classical techniques recommends three precipitations with hydrogen sulfide to effect and acceptable separation. Even then there is no assurance that the separation is completely quantitative.

In this work, only a single precipitation of each element is made. With both cadmium and zinc being finally determined as their respective sulfates, it makes little difference if either is contaminated with traces of the other, providing the trace* content of each in the other may easily be determined. This is accomplished quantitatively with atomic absorption spectrophotometry.

Atomic Absorption Spectrophotometric Analysis of Cadmium and Zinc Sulfate Residues

Except for the necessity of making proper standard adjustments for the matrix effect of cadmium on the absorbance of traces of zinc and of zinc on the absorbance of traces of cadmium, the atomic absorption spectrophotometric technique applies directly to the gravimetric cadmium and zinc sulfate residues. By providing accurate correctional data for both cadmium and zinc, it improves the accuracy and enhances the reliability of the gravimetric procedure.

Although many corrections are too small to have gravimetric significance, samples 5 and 6 in Table 4 show a considerable amount of zinc in the cadmium sulfate residue. These particular samples each contained 0.1000 g of phosphorus to simulate a cadmium-zinc arsenide-phosphide crystal. In addition, they contained relatively large amounts of zinc. Since atomic absorption spectrophotometry provides proper and accurate adjustment for the presence of zinc, no effort was made to investigate the matter further.

*Polarographically, traces of cadmium in zinc may be easily determined because the cadmium half-wave precedes that of zinc. Polarography is not recommended for the determination of traces of zinc in cadmium.

Table 4
Atomic Absorption Spectroscopic Analysis of
Cadmium and Zinc Sulfate Residues

Sample Number	Cadmium Sulfate Residue		Zinc Sulfate Residue	
	Cadmium Present (g)	Zinc Present (g)	Zinc Present (g)	Cadmium Present (g)
1	0.1840	0.00048	0.0171	0.00027
2	0.1730	0.00078	0.0233	0.00046
3	0.1190	0.00095	0.0518	0.00007
4	0.1820	0.00084	0.0050	0.00026
5	0.1720	0.0120*	0.1520	0.00022
6	0.1850	0.0180*	0.1480	0.00014

*Synthetic standard contained 0.1000 g of phosphorus and relatively large amounts of zinc.

Polarographic Determination of Cadmium and Zinc

For the ranges of cadmium and zinc encountered in the synthetic standard sample solutions, the 1M ammonium hydroxide-ammonium chloride provided better polarograms than most of the supporting electrolytes tested. Working at a final volume of 50 ml, the sample aliquots electrolyzed contained both cadmium and zinc in amounts varying between 1000 and 4000 μg. Optimum recorder scale coverage was obtained by using damped electrolyzing current-range settings of 10, 20, and 30 μA as required.

It was found essential that the standards used to prepare the polarographic calibration curve be given the same sulfuric acid fuming treatment as was given the samples to be tested. Otherwise the slope of the residual and limiting current traces was greater for the calibration-curve standards than for the samples being tested.

Although the polarograms obtained for the various sample solutions were well defined and easily measurable, considerable variation exists among some of the data. This may be due in part to slight inaccuracies in measuring the diffusion currents and to the multiplying factor of 50 required to determine the total cadmium and zinc sample content. No attempt has been made to determine the cause of the bias (on the high side) that exists among the cadmium polarographic data (see Table 1).

Referring to Table 1, the percent found column is a rather severe way of presenting data. For example, a sample-found value of 0.0415 g represents a 98.8% recovery on a sample-taken value of 0.0420 g. In this instance an absolute error of 0.0005 g is involved.

SUMMARY

The reduction, distillation, and determination of arsenic has been carefully investigated in this study. Its quantitative isolation is required to assure the successful subsequent wet-chemical or instrumental determination of cadmium. A combined wet-chemical and atomic absorption spectrophotometric procedure is presented for the accurate gravimetric determination of both cadmium and zinc. A polarographic procedure is presented that will satisfy many analytical requirements.

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13. ABSTRACT

Cadmium-zinc arsenide has been analyzed by a combination of chemical and instrumental techniques. After the initial removal of arsenic by distillation, cadmium and zinc are determined by a combined gravimetric and atomic absorption spectrophotometric procedure or by a polarographic procedure.

The experimental procedures for determining each of the three major constituents are given in detail. Methods used for checking the effectiveness of their respective separation are also discussed.

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